

VIRIAL COEFFICIENTS FOR THE LENNARD-JONES GAS

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One of the earliest methods of calculation of the third virial coefficient for the Lennard-Jones (12,6) potential used the three-dimensional Fourier transform of the Mayer function

$$f(r) = \exp\{-V(r)/kT\} - 1. \quad (1)$$

As the third virial coefficient is simply a three-sided ring integral, Montroll and Mayer¹ showed that it was just proportional to the integral of the cube of the Fourier transform. The Lennard-Jones potential required a numerical evaluation of the transform and a resulting numerical integration.

In their numerical calculations by a different method, Bird, Spotz, and Hirschfelder² noticed discrepancies between their results and the original calculations of Montroll and Mayer.¹ We have calculated numerically the third virial coefficients for the (12,6) potential by the Fourier transform method and obtained results which remove these discrepancies, especially for the larger values of the reduced temperature $\tau = kT/\epsilon$. Both calculations are given in Table I.

The calculated Fourier transforms are themselves of interest for other reasons. The Fourier transform is the first iterate in the method

proposed by Van Leeuwen, Groeneveld, and DeBoer³ for solution of the integral equation for the radial distribution function in the convolution, hypernetted chain approximation (C.H.N.C.).⁴ The original purpose in calculating the Fourier transforms was to obtain the first iterate for solving the integral equation. The calculation of the third virial coefficient would provide an indication of the accuracy of the calculation of the first iterate.

The transforms have also been used to evaluate the "ring" contributions to higher virial coefficients. In particular, they yield an indication of the accuracy of several recent calculations of the fourth virial coefficient. As summarized in Table II, these results indicate closer agreement with the Legendre expansion method of Barker and Monaghan,^{5,6} than with the Gaussian method of Boys and Shavitt.⁷ As the latter noticed in their calculation of the third virial coefficient, there appears to be an optimum number of terms in the Gaussian expansion of the Mayer function beyond which the results for the virial coefficients become worse.

Ring contributions to third and higher virial coefficients for this and other potentials, as well as the Fourier transforms,⁸ will be published later.

Table I. Third Virial Coefficient, $C^*(\tau)$ for
a (12,6) Lennard-Jones Potential

τ	Present Calculation Using Three-Dimensional Fourier Transforms	Numerical Integration of Bird, Spotz, and Hirschfelder (2)
400.0	0.078627	0.07862
100.0	0.14253	0.14251
50.0	0.18525	0.18529
20.0	0.24644	0.24643
10.0	0.28602	0.28610
8.0	0.29608	0.29618
6.0	0.30761	0.30771
5.0	0.31508	0.31508
4.0	0.32664	0.32662
3.0	0.35229	0.35234
2.5	0.38091	0.38108
2.0	0.43698	0.43710
1.6	0.51799	0.51803
1.4	0.56831	0.56831
1.2	0.59229	0.59240
1.0	0.42878	0.42966
0.7	-3.3863	-3.37664

Table II. "Ring" Contribution $D_1^*(\tau)$ to the
Fourth Virial Coefficient for a
(12,6) Lennard-Jones Potential

τ	Present Calculation	Legendre Expansion (Ref. 5)	Gaussian Expansion (Ref. 7) [*]
400.0	- 0.043946		
100.0	- 0.10571		
50.0	- 0.15454		- .230 (3)
20.0	- 0.23027	- 0.2309	- .226 (4)
10.0	- 0.27805		- .228 (5)
8.0	- 0.28902	- 0.2900	- .226 (6)
6.0	- 0.30106		- .300 (3)
5.0	- 0.30931		- .286 (4)
4.0	- 0.32385	- 0.3217	- .282 (5)
3.0	- 0.36061		- .281 (6)
2.5	- 0.40432		- .350 (3)
2.0	- 0.50224	- 0.5013	- .326 (4)
1.6	- 0.72731		- .300 (5)
1.4	- 1.04049		- .293 (6)
1.2	- 1.8967	- 1.9033	- .579 (3)
1.0	- 5.0183		- .530 (4)
0.7	- 55.862		- .468 (5)
			- .450 (6)

^{*}The number in parenthesis after the value indicates the number of terms in the expansion.

FOOTNOTES

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